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(54) Title: WELL SERVICING FLUIDS

(57) Abstract

This invention relates to an aqueous well servicing fluid comprising in solution a cesium salt of a carboxylic acid characterised in that the carboxylic acid has: a) at least one carboxyl group and b) at least one other carboxyl and/or hydroxy group. Typical examples are cesium lactate, citrate and oxalate. Use of these cesium salts enables the production of dense brines usable as well servicing fluids.

WELL SERVICING FLUIDS

The present invention relates to a composition for and method of enhancing the density of well servicing fluids prepared therefrom.

It is well known that aqueous media, especially those containing oil field brines, are generally used as well servicing fluids such as drilling fluids, completion fluids, packer fluids, well treating fluids, subterranean formation testing fluids, spacer fluids and hole abandonment fluids. For all these uses, such brines desirably have relatively high density. In order to achieve this, various components have been added to such fluids. Examples of such additives include heavy brines such as zinc bromide or combinations thereof with eg hydrophilic polymeric materials such as hydroxyethyl cellulose. One of the problems with such brines currently used is that they contain zinc atoms which are not environmentally friendly. Moreover, the polymeric hydroxyethyl celluloses are poorly hydrated, solvated or dispersed in aqueous systems which contain water-soluble salts of multivalent metals. In order to overcome the problems of toxicity it is now proposed to use a non-toxic halide.

It is an object of the present invention to devise a composition which provides the desired high density aqueous brine systems which are of much lower ecotoxicity.

Accordingly, the present invention is an aqueous well servicing fluid comprising in solution a cesium salt of a carboxylic acid characterised in that the carboxylic acid has:

a) at least one carboxyl group and

b) at least one other carboxyl and/or hydroxy group.

Thus the cesium carboxylate used in the well servicing fluids of the present invention may be derived from simple di- or polycarboxylic acids or from the corresponding hydroxycarboxylic acids. The carboxylic acids are suitably aliphatic and saturated and can be selected from oxalic acid, malonic acid, succinic acid, adipic acid, lactic acid (also known as 2-hydroxy propionic acid), citric acid (also known as 2-hydroxy-1,2,3-propane-tricarboxylic acid) and tartaric acid (also known as 2,3-dihydroxybutanedioic acid). Of these, the preferred salts are cesium oxalate, cesium lactate, cesium citrate and cesium tartarate. A surprising feature of the present invention is that these cesium carboxylates even when used singly provide a density ranging from 1.6 - 2.63g/cm^3. This is therefore a most desirable density enhancing compound for well servicing fluids and the salts are environmentally safe and are user friendly.

The amount of cesium carboxylates used in a formulation for well servicing fluids can be readily determined. The simplicity of the invention should ensure that these values can be readily established by simple experiments. An important consequence of this invention is that it enables lower concentrations of the relatively expensive cesium carboxylates to be used in the composition to achieve the desired densities in the well servicing fluids.

Optionally, the cesium carboxylates such as eg cesium oxalate or citrate can be used in combination with other alkali metal salts eg the carboxylates of potassium, sodium and/or cesium including the simple acetates and formates in aqueous brines. By varying the relative concentrations of the carboxylic acid salts in the fluid it is possible to achieve the desired density of the brine or the ultimate servicing fluid in which the brine is used. Thus densities ranging from 1.6 to 2.63 g/cm^3, preferably from 1.8 to 2.5 g/cm^3 can be achieved using the compositions of the present invention.

The well servicing fluids of the present invention can be prepared by mixing aqueous solutions of the individual salts. Alternatively, a mixture of the aqueous solutions of the respective bases of the alkali metals can first be prepared to which the desired carboxylic acid is added to form the respective carboxylates. The desired concentration of the respective salts in the aqueous solution so formed can be adjusted by evaporation of the water from the mixed solution.

The present invention is further illustrated with reference to the following Examples:

EXAMPLES:

A number of organic cesium salts were prepared from a 50% w/w cesium hydroxide solution, by the addition of an organic acid. After reaction and at a final pH of 7-8, the mixture was heated and the by- product, water, was evaported until a saturated solution of the cesium carboxylate was obtained. During the evaporation step, samples were taken, cooled to ambient temprature (ca.25°C) and densities and concentrations measured. From the saturated solution solutions, the clear upper layers were taken and used as the cesium carboxylate liquid. The salt concentration in this liquid was determined by gravimetric analysis and by subtraction of the water content of the sample. The water content was determined by Karl Fischer titration.

The results of the above Examples with various salts are tabulated below:

1. Cesium citrate:

Conc (%w/w) of Cs salt	Conc of Cs (%w/w)	Density (g/cm^3)
51.8	35.1	1.65
68.7	46.6	2.00
78.8	53.4	2.28
89.2	60.5	2.63*

* - a very viscous solution

2. Cesium lactate:

Conc (% w/w) Cs-salt	Conc (% w/w) Cs	Density (g/cm^3)
54.9	32.9	1.53
66.0	39.5	1.69
75.9	45.5	1.87
89.5	53.6	2.12*

* - a viscous solution

3. In a further experiment, cesium oxalate was used and showed that at a cesium salt concentration of 72.8% w/w, it had a cesium concentration of 54.7% w/w and a density of 2.17 g/cm^3.

In view of the comparative non-ecotoxicity of these materials such cesium carboxylates are extremely valuable additives for producing heavy brines.

Claims:

1. An aqueous well servicing fluid comprising in solution a cesium salt of a carboxylic acid characterised in that the carboxylic acid has:

a) at least one carboxyl group and

b) at least one other carboxyl and/or hydroxy group.

2. An aqueous well servicing fluid according to Claim 1 wherein the cesium carboxylate is derived from simple di- or polycarboxylic acids or from the corresponding hydroxycarboxylic acids.

3. An aqueous well servicing fluid according to Claim 1 or 2 wherein the carboxylic acids are suitably aliphatic and saturated and are selected from the group consisting of oxalic acid, malonic acid, succinic acid, adipic acid, lactic acid (also known as 2-hydroxy propionic acid), citric acid (also known as 2-hydroxy-1,2,3-propane-tricarboxylic acid) and tartaric acid (also known as 2,3-dihydroxybutanedioic acid).

4. An aqueous well servicing fluid according to any one of the preceding Claims wherein the cesium salt is cesium oxalate, cesium lactate, cesium citrate or cesium tartarate.

5. An aqueous well servicing fluid according to any one of the preceding Claims wherein said fluid comprising a cesium carboxylate has a density ranging from 1.6 - 2.63g/cm^3.

6. An aqueous well servicing fluid according to any one of the preceding Claims wherein the fluid comprises carboxylates of potassium, sodium and/or cesium.

7. An aqueous well servicing fluid according to Claim 6 wherein the carboxylates of sodium and potassium are the acetates and formates.

8. A aqueous well servicing fluid according to any one of the preceding Claims wherein the fluid is prepared by mixing aqueous solutions of either the individual salts, or, the respective bases of the alkali metals to which the desired carboxylic acid is added to form the respective carboxylates.

INTERNATIONAL SEARCH REPORT

Interna. al Application No
PCT/GB 95/00206

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 572 113 (BP CHEMICALS LIMITED) 1 December 1993 see page 2, line 15 - line 41 see examples 1-4	1-8
Y,P	GB,A,2 277 338 (BP EXPLORATING COMPANY) 26 October 1994 see page 3, line 7 - page 4, line 9; claims 1-3	1-8
Y	EP,A,0 137 872 (HALLIBURTON) 24 April 1985 see page 3, line 13 - page 4, line 1 see page 5, line 15 - page 7, line 12	1-8
A	GB,A,2 251 876 (EXXON) 22 July 1992 see claims 1-8	6,7

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
10 April 1995	03. 05. 95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Boulon, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 81-94446D & SU,A,812 823 (BOREHOLE REINFORCE) 15 March 1981 see abstract ---	6,7
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 92-413409 & SU,A,1 685 971 (MOSC GUBKIN OIL GAS INST) 23 October 1991 see abstract -----	6,7

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EP-A-0137872	24-04-85	NONE	
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